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(71) Applicant
Dow Deutschland Inc

(Incorporated in the Federal Republic of Germany)

**PO Box 1120, 2160 Stade,
Federal Republic of Germany**

(72) Inventors
**Marian Bujara
Juergen Hermanns
Heinz Groenewald
Egon Oelrich
Hans-Peter Schneider**

(74) Agent and/or Address for Service
**W H Beck, Greener & Co
7 Stone Buildings, Lincoln's Inn, London, WC2A 3SZ,
United Kingdom**

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GB 1165824 A GB 0804306 A GB 0710121 A

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(54) **Process for grinding cellulose compounds**

(57) In a process for grinding a cellulose compound, the compound having a water content of from 30 to 80 wt.-%, based on wet compound, and a temperature of from 40 to 120°C is gelled and cooled to a temperature of from -10 to 100°C and subsequently dried and ground. By the gelation the bulk density of the ground cellulose compound is increased, compared to a ground cellulose compound which has not been subjected to a precedent gelation step.

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PROCESS FOR GRINDING CELLULOSE COMPOUNDSBackground of the Invention

5 The present invention relates to a process for grinding cellulose compounds. Cellulose compounds, such as cellulose ethers are frequently used in various applications, for example as thickeners, adhesives, moisture retention aids or surfactants. Due to their various uses, cellulose compounds such as cellulose
10 ethers are commercially available in wide ranges of substitution levels and molecular weights. The cellulose ethers are generally produced in an aqueous reaction medium. After the reaction and after an optional purification step the cellulose ethers are
15 obtained in the form of crumbles or lumps or in a fibrous or fluffy structure. Usually the produced cellulose ethers have a relatively high water content. The cellulose ethers are generally not useful in these forms in the applications listed above. Nearly all
20 cellulose ethers have to be ground and dried to make them useful for the stated applications.

25 Methods of grinding and drying cellulose ethers have been known for a long time.

DE-A-2,458,998 (equivalent to U.S. patent 4,076,935) relates to a grinding method wherein a cellulose compound having a water content of 5 to 14 wt.-% is ground in a vibration mill in contact with air and with sufficient water to yield a product having a water content of 2 to 10 wt.-%.

U.S. patent 4,044,198 discloses a method for cold-milling cellulose derivatives. In the discussion of the prior art the patent discloses that finely pulverized and pourable methyl cellulose products so far have been produced by washing the raw product obtained in the etherification process nearly salt-free with hot water, drying it by centrifuging at a high temperature to 50% by weight of water, based on wet methyl cellulose, and premixing the product obtained by kneading it with water at standard temperature (20°C), i.e. causing it to start to gelatinize, until the product has a water content of 60 to 70 wt.-% (based on wet substance), followed by densification, granulation, drying, milling and sorting. The U.S. patent discloses that, apart from the circumstantial preparation of the material for actual milling, the degree of fineness is relatively low with this known method. Accordingly, U.S. patent 4,044,198 suggests to cool a cellulose derivative which is soluble or swellable in water and has a water content of between 40 and 150%, based on its dry weight, by means of liquid nitrogen until it becomes brittle and the thus cooled cellulose derivative is milled in a mill. The cellulose derivative is embrittled when it has been cooled below its glass transition temperature. The U.S. patent discloses that the disclosed cold-milling method can be

employed after it has been densified and granulated in known manner, for example in order to obtain a ground product having a higher bulk density.

5 Various densification methods have been
suggested in the prior art. German patent 952,264
discloses a method of converting a moist methyl
cellulose ether into a powder which is rapidly soluble
in water. Methyl cellulose ether having a water
10 content of 50-70 wt.-% is first homogenized under
pressure to a plastified mass, ground in a hammer mill
and dried in a circulating air drier. DE-A-3,032,778
suggests a method of continuous homogenization,
pelletization and drying of cellulose ethers wherein a
15 cellulose ether having a moisture content of from 35 to
45 wt.-% is subjected to cutting, impact and shear
actions and homogenized. The cutting, impact and shear
actions are provided by revolving bodies which rotate at
different speeds. DE-A-1,454,824 discloses a process
20 for producing granules or powders from fibrous, dry
cellulose ethers wherein the fibrous cellulose ether is
passed through two smooth frictioning rolls and pressed
to a mat. The mat is removed from the rolls, partially
25 broken and then ground to granules or a powder.
However, it is well known that mechanical stress of the
cellulose ether during the densification of the
cellulose ether by homogenization, plastification or
pressure to form a mat is so high that during the
30 grinding step the chain length of the cellulose ether
molecules is reduced. This degradation results in a
substantial viscosity loss of the ground cellulose
ether, compared to the crude cellulose ether prior to
grinding. A viscosity loss is undesirable in many
applications of the cellulose ether. Furthermore, the

equipment needed for homogenization, plastification or forming a mat of the cellulose ether, such as an extruder or a screw press, are very expensive and require a great deal of energy in operation.

5 U.S. patent 4,820,813 suggests to grind a cellulose ether in a high speed air swept impact mill instead of in a standard ball mill in order to minimize the viscosity loss of the cellulose ether.
10 Unfortunately, the U.S. patent is silent about the bulk density of the ground product.

EP-A 0,049,815 (equivalent to U.S. patent 4,415,124) also addresses to the problem of viscosity
15 loss during the grinding step. It suggests a method of producing micropowders from cellulose ethers having a fine-fiber, cottony or wooly structure. According to this method the cellulose ether is consolidated or embrittled in a cooled vibration or ball mill or a
20 pellet press. The consolidated or embrittled material is then ground in a jet mill, a pin mill or an impact disk mill. The normal degradation of the cellulose ether macromolecules is only from 2-25%. Unfortunately,
25 the suggested process is expensive because two different mills or a mill and a pellet press are required.

In view of these deficiencies of the methods of
30 the prior art EP-A-0,370,447 (equivalent to U.S. patent 4,979,681) suggests simultaneous grinding and drying of moist cellulose ethers in a special equipment wherein moist cellulose ether is impact-comminuted while being circulated and simultaneously friction-comminuted in the opposite direction to that of the impact-

comminution. EP-A-0,370,447 claims that in the disclosed method controlled degrees of grinding can be set, the products do not become horny, only a small residual moisture content remains after grinding, the bulk density of the product is increased and only a minimum degradation in viscosity or none at all as compared with the starting products takes place. Unfortunately, the disclosed process can only be conducted in a very special equipment.

Accordingly, it is still desirable to provide a new process for grinding a cellulose compound.

Specifically, it is desirable to provide a grinding process which does not contain a densification step by homogenization, plastification or pressure to form a mat and wherein only a minimum degradation of the cellulose compound in viscosity as compared with the starting products takes place. Furthermore, it is desirable to provide a grinding process wherein a cellulose compound of high bulk density is obtained because a high bulk density facilitates its storage and dosage. It is also desirable to provide a grinding process which does not require the construction and use of specialized equipment, but which can be conducted in various apparatuses which are commercially available.

Summary of the Invention

The ~~present invention relates~~ to a process for grinding a cellulose compound wherein the cellulose compound having a water content of from 30 to 80 wt.-%, based on wet compound, and a temperature of from 40 to

120°C is gelled and cooled to a temperature of from -10 to 100 °C and subsequently dried and ground.

5 Surprisingly, it has been found that cellulose compounds of higher bulk density are obtained when the cellulose compounds are gelled and cooled before they are dried and ground, as compared with cellulose compounds which are dried and ground in the same manner but not gelled.

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Detailed Description of the Invention

15 The process of the present invention may be used for the comminution of cellulose compounds, such as cellulose or ether derivatives thereof, for example alkyl, hydroxyalkyl, alkylhydroxyalkyl and carboxyalkyl cellulose ethers and mixed ethers of cellulose and carboxyalkyl cellulose either alone or in admixture.

20 Useful cellulose ethers are for example C₁₋₂-alkyl cellulose ethers, such as methyl cellulose ethers or ethyl cellulose ethers, or hydroxy-C₂₋₄-alkyl C₁₋₂-alkyl cellulose ethers, such as hydroxypropyl methyl

25 cellulose ethers, hydroxypropyl ethyl cellulose ethers, hydroxybutyl methyl cellulose ethers, hydroxyethyl methyl cellulose ethers or hydroxyethyl ethyl cellulose ethers. Methyl cellulose ethers and hydroxypropyl methyl cellulose ethers are preferred. The levels of

30 substitution of the cellulose ethers can vary in a wide range. The methyl cellulose ethers generally have a methoxyl substitution of from 10 to 40 percent, preferably from 15 to 35 percent, more preferably from 25 to 35 percent. The methoxyl substitution is measured and calculated according to ASTM D 3876. The

hydroxypropyl methyl cellulose ethers generally have a methoxyl substitution of from 1 to 40 percent, preferably from 10 to 40 percent, most preferably from 15 to 35 percent and a hydroxypropoxyl substitution of from 2 to 40 percent, preferably from 4 to 40 percent and most preferably from 4 to 35 percent. The methoxyl and hydroxypropoxyl substitutions are measured and calculated according to ASTM-D 1347-72 and ASTM D 2363-72, respectively. All the percentages of substitution are by weight of the finally substituted material. The cellulose ethers preferably have a viscosity of from 1 to $10 \cdot 10^6$ cps, more preferably from 3 to 500,000 cps, most preferably from 50 to 200,000 cps, as a 2 weight percent solution in water as calculated or measured using an UBBELOHDE viscosimeter at 20°C. The advantage of the gelling/cooling step in the process of the present invention is most readily apparent when the process is applied to methyl cellulose ethers or to low or medium substituted hydroxypropyl methyl cellulose ethers which have a total of hydroxypropoxyl and methoxyl substitution of up to 40%. Such cellulose ethers often exhibit a fluffy structure before they are treated according to the process of the present invention. When such cellulose ethers are ground without precedent gelling, often a product of undesirably low bulk density is obtained. Cellulose ethers may be produced by known methods, for example as described in U.S. patents 2,831,852; 2,949,452; 3,388,082; 4,410,693 and 4,456,751. After the etherification of the cellulose the produced cellulose ether is usually washed with hot water. After the washing step the cellulose ether generally has a temperature and a water content that it can be subjected to the gelling and cooling step in the

process of the present invention without any pretreatment.

5 The cellulose compound, such as cellulose or a cellulose ether, should have a water content of from 30 to 80 wt.-%, based on wet compound, before it is subjected to the gelling and cooling step. If its water content is higher, it should be pre-dried until its water content is within the mentioned range. The
10 water content of the cellulose compound preferably is from 30 to 70 wt.-%, more preferably from 40 to 60 wt.-%, based on wet compound. The temperature of the cellulose ether prior to gelling is from 40 to 120°C, preferably from 60 to 120°C, more preferably from 80 to
15 110°C.

Gelling of the cellulose compound is generally achieved by cooling, preferably under agitation. Depending on the water content of the cellulose
20 compound, for example if the cellulose ether has a water content of about 70 wt.-% or more, gelling of the cellulose compound may be achieved without cooling. In this case the cellulose compound can be cooled after
25 gelling. However, in many cases the cellulose compound only gels upon cooling. Accordingly, the cellulose compound is preferably gelled during cooling. Most preferably, the cellulose compound is gelled by continuous agitation and cooling. The cellulose
30 compound is cooled to a temperature of from -10 to 100°C, preferably of from -10 to 60°C, more preferably of from 0 to 50 °C. It is essential that the cellulose compound loses its fibrous structure during gelling. The gelling can be achieved and controlled by selecting and controlling the water content of the cellulose

compound to be gelled, the extent of cooling and the extent of agitation. Sufficient gelling can be monitored by physical means. For example, the skilled artisan can examine by light microscopy whether the cellulose compound has lost its fibrous structure.

5 According to another method, a sample of the cellulose ether is subjected to a pressure of about 100 bar; sufficient gelling is achieved if the pressed sample of about 0.3 mm thickness is transparent. Preferably, no

10 additional amount of water is added to the cellulose ether during gelling such that the water content of the cellulose compound after gelling generally is from 30 to 80 wt.-%, preferably from 30 to 70 wt.-%, more preferably from 40 to 60 wt.-%, based on wet compound.

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Advantageously, the cellulose compound is gelled in an agitation machine. Agitation machines are well known in the art. The gelling is preferably conducted in an agitation machine that enables

20 continuous agitation and cooling and allows the application of shear stress to the cellulose compound. Suitable agitation machines are for example stirred vessels, paddle mixers, screw mixers, plough share

25 mixers, ribbon mixers, or cone mixers. Preferably, these mixers are cooled. The cooling of the cellulose compound can for example be effected by means of a cooling jacket and/or by purging a cooling gas through the agitation machine.

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After gelling and cooling the cellulose compound is dried and ground without applying an intermediate densification and granulation step. The drying and grinding of the cellulose compound can be conducted in a known manner in any mill that does not

cause a substantial degradation of the viscosity of the cellulose compound. Such mills are well known in the art and commercially available. Useful mills are for example hammer mills, impact mills, such as a high speed air swept impact mill described in U.S. patent 4,820,813, grinding and drying equipment described in U.S. patent 4,979,681 and convection whirl dryers described by K. Kröll, "Trockner und Trocknungsverfahren", volume 2, pages 313-318, 2nd edition, Springer-Verlag, Berlin Heidelberg New York 1978. Ball mills are less suitable. Although the drying and grinding of the cellulose compound may be conducted separately, the gelled cellulose compound is preferably dried and ground simultaneously.

Simultaneous drying and grinding is well known in the art and for example described by F. Sass, C. Bouche in "Dubbel's Taschenbuch für den Maschinenbau, vol. 2, Berlin 1958, pages 19 etc. Machines for simultaneous drying and grinding are commercially available and for example described in Altenburger Maschinen KG in "Die Chemische Produktion", vol. 9, edition 6/80, 1980.

In a preferred embodiment of drying and grinding, the gelled and cooled cellulose ether is fed into the housing of an impact mill in a known manner, for example via a screw conveyer. In the impact mill the cellulose compound is preferably conveyed by a gas stream, such as air, onto a rotating rotor equipped with grinding bars. The cellulose compound may be smoothly ground by impact which is generated by turbulences in the space between the rotating bars and the housing. The ratio between the gas flow and the weight of the cellulose ether preferably is from 10 to 50 m³/kg, more preferably from 15 to 45 m³/kg. The

temperature of the gas stream generally is from 20 to 250°C, preferably from 20 to 200°C, more preferably from 20 to 150°C. Preferably, the impact mill is run at a circumferential speed of 50 to 160 m/s, more preferably from 80 to 140 m/s. If desired, the ground material can be sieved and the material of too large particle size can be recycled to the mill. The average particle size generally is of from 5 to 1000 micrometers, preferably from 10 to 600 micrometers.

Due to the gelling step in the process of the present invention the bulk density of the ground cellulose compound generally is at least 5%, often at least 20% and in many cases even at least 50 percent higher than the bulk density of a cellulose compound which has been ground in the same manner but which has not been caused to gel. The gelling and cooling as well as the drying and grinding of the cellulose compound can be conducted in known, relatively inexpensive equipment. Further, the process of the present invention does not make use of a densification step by homogenization, plastification or pressure. The viscosity loss of the cellulose compound is generally less than 15 %, often even less than 10 %, and in many cases even less than 5 %.

The process of the present invention is further illustrated by the following examples which are not to be construed to limit the scope of the invention. Unless otherwise mentioned, all parts and percentages are by weight. The viscosities of the cellulose ethers stated below relate to a 2 weight percent solution of the cellulose ether in water as measured using an UBELLOHDE viscosimeter at 20°C.

Example 1

5 A hydroxypropyl methyl cellulose ether A having
a hydroxypropoxyl substitution of 24%, a methoxyl
substitution of 20%, a viscosity of 75,000 cps, a water
content of 45%, based on wet compound, and a
temperature of 80°C is divided into two portions. The
10 first, comparative portion is left without further
treatment for grinding. The second portion is cooled
to 25 °C in a ribbon mixer. During blending and
cooling the cellulose ether of the second portion is
gelled. The water content prior to and after gelling
15 is 45%, based on wet compound.

The two portions are separately ground in an
impact mill. Both portions are ground and dried at a
ratio between air flow and weight of cellulose ether of
20 25 m³/kg and at an air temperature of 200 °C. The
ground comparative portion has a residual water content
of 3%, an average particle size of 60 micrometers, a
viscosity of 69,000 cps and a bulk density of 520 g/l.
25 The ground portion according to Example 1 has a
residual water content of 3 %, an average particle size
of 55 micrometers, a viscosity of 72,000 cps and a bulk
density of 560 g/l.

Example 2

30 Example 1 is repeated using a hydroxypropyl
methyl cellulose ether B having a hydroxypropoxyl
substitution of 10%, a methoxyl substitution of 29%, a
viscosity of 4,000 cps, a water content of 45%, based

on wet compound, and a temperature of 80°C. The ground comparative portion has a residual water content of 3%, an average particle size of 75 micrometers, a viscosity of 3,600 cps and a bulk density of 450 g/l. The ground portion according to Example 2 has a residual water
5 content of 3 %, an average particle size of 80 micrometers, a viscosity of 3,800 cps and a bulk density of 620 g/l.

10 Example 3

Example 1 is repeated using a methyl cellulose ether C having a methoxyl substitution of 28%, a viscosity of 20,000 cps, a water content of 55 %, based
15 on wet compound, and a temperature of 80°C. The ground comparative portion has a residual water content of 4%, an average particle size of 56 micrometers, a viscosity of 18,000 cps and a bulk density of 170 g/l. The ground portion according to Example 3 has a residual water
20 content of 4.5%, an average particle size of 50 micrometers, a viscosity of 17,500 cps and a bulk density of 270 g/l.

25 Example 4

Example 1 is repeated using a hydroxypropyl methyl cellulose ether D having a hydroxypropoxyl substitution of 10%, a methoxyl substitution of 22%, a
30 viscosity of 100,000 cps, a water content of 40%, based on wet compound, and a temperature of 90°C. The ground comparative portion has a residual water content of 4 %, an average particle size of 75 micrometers, a viscosity of 80,000 cps and a bulk density of 180 g/l. The ground portion according to Example 4 has a

residual water content of 4.5 %, an average particle size of 60 micrometers, a viscosity of 90,000^{cps} and a bulk density of 350 g/l.

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CLAIMS:

1. A process for grinding a cellulose compound wherein the cellulose compound having a water content of from 30 to 80 wt.-%, based on wet compound, and a temperature of from 40 to 120°C is gelled and cooled to a temperature of from -10 to 100°C and subsequently dried and ground.
2. A process of Claim 1, wherein the cellulose compound is a cellulose ether.
3. A process of Claim 2, wherein the cellulose compound is a methyl cellulose ether or hydroxypropyl-methyl cellulose ether having a total hydroxypropyl and methoxyl substitution of up to 40%.
4. A process of any one of Claims 1 to 3, wherein the cellulose compound is gelled in an agitation machine.
5. A process of any one of Claims 1 to 4, wherein the cellulose compound is gelled during cooling.
6. A process of Claim 5, wherein the cellulose compound is gelled and cooled in a cooled agitation machine.
7. A process of any one of Claims 1 to 6, wherein the temperature of the cellulose compound is from 60 to 120°C prior to gelling and from -10 to 60°C after gelling.
8. A process of Claim 7, wherein the temperature of the cellulose compound is from 80 to 110°C prior to gelling and from 0 to 50°C after gelling.
9. A process of any one of Claims 1 to 8, wherein the cellulose compound has a water content of from 30 to 70

wt.-%, based on wet compound.

10. A process of Claim 9, wherein the water content is 40 to 60 wt.-% based on wet cellulose compound.

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11. A process of any one of Claims 1 to 10, wherein the gelled cellulose compound is simultaneously dried and ground.

10 12. A process of any one of Claims 1 to 11, wherein the gelled cellulose compound is dried and ground in an impact mill.

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Patents Act 1977

Examiner's report to the Comptroller under
Section 17 (The Search Report)

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Relevant Technical fields

(i) UK CI (Edition K) C3A

(ii) Int CI (Edition 5) C08B

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K MACDONALD

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

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26 NOVEMBER 1992

Documents considered relevant following a search in respect of claims 1-12

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1165824 (ICI) eg Example 1	at least Claim 1
X	GB 804306 (DOW CHEMICAL) page 2 lines 18-114	at least Claim 1
X	GB 710121 (ICI) Example 1; page 1 lines 48-49	at least Claim 1

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

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